

CATALYTIC PARTIAL OXIDATION OF METHANE TO HIGHER HYDROCARBONS

R.J. Tyler and C.A. Lukey

CSIRO Division of Fossil Fuels, PO Box 136, North Ryde, NSW 2113, Australia

1. INTRODUCTION

The direct conversion of methane to higher hydrocarbons such as ethylene is currently a very active research area. Olefins are of particular importance as they represent intermediates suitable for oligomerisation to transport fuels. Jones et al. (1) recently reviewed the potential for methane conversion and described results using Mn-based redox type catalysts in both cyclical (using air and methane alternately) and continuous reactors. Bytyn and Baerns (2) reported the activity of PbO-based catalysts and concluded that the acidity of the surface influences the reaction pathway, with high acidity resulting in poor selectivity to the desired hydrocarbons. Otsuka et al. (3,4) described results for a variety of catalysts including rare earths, transition metal elements, alkali and alkaline earth compounds and halide doped mixtures. Lunsford et al. (5,6) were the first to report the use of a Li-doped magnesia and postulate that methane activation occurred at $[Li^+O^-]$ centres. This catalyst is notable in that it does not contain metal ions of variable oxidation state and the active species is thought to involve the anion. A remarkable feature of the published data is the variety of surfaces that promote the reaction and the similarity of many of the reported product distributions. This suggests that after the initiation step the hydrocarbon building steps probably occur via a gas phase mechanism (1).

The present paper reports results obtained using a Li/MgO catalyst with CH_4/O_2 mixtures and describes the influence of contact time and oxygen concentration on reaction rate and product selectivities. Implications for the reaction mechanism are also discussed.

2. EXPERIMENTAL

Catalysts were prepared by procedures similar to those described by Ito and Lunsford (5) and calcined in air at 850°C before use. Initial Li loadings were equivalent to a Li/Mg atomic ratio of 0.58. However subsequent analysis showed substantial loss on firing and to some extent during reaction.

Experiments were conducted using quartz or alumina fixed-bed reactors and a continuous flow of feed gas. Pseudo-contact times (W/F) equivalent to the weight of catalyst (g) divided by the feed gas flowrate at operating conditions ($ml\ s^{-1}$) were varied in the range 0.01 to 2. Temperatures were in the range 550 to 850°C. Exit gas analysis was performed by gas chromatography (hydrocarbons) and continuous gas analysers (CO , CO_2 and O_2). In some experiments water analyses were also carried out enabling oxygen balances to be determined (usually $100 \pm 5\%$) and hydrogen yields to be calculated from a hydrogen balance. Confirmation of hydrogen yields by analysis was obtained in selected experiments.

3. RESULTS AND DISCUSSION

3.1 Reaction rates

Figure 1 shows the dependence of the methane conversion rate ($mmol\ CH_4\ min^{-1}\ g^{-1}$ catalyst) on the pseudo-contact time (W/F) for a range of O_2 concentrations using 17.3 g of catalyst at 770°C. The methane content of the feed gas was held constant at 90% and the oxygen concentration was varied between 1 and 9.4% with the balance being nitrogen.

As expected, the methane conversion rate increased as the level of oxygen in the feed gas increased. However, for each oxygen level there was a marked decline in

methane conversion rate as the contact time increased (i.e. as the gas velocity through the reactor decreased). The possibility that this effect was caused by limitations in the mass transfer of reactants across the boundary layer to the external surface of the catalyst was checked using standard calculation procedures (7). In all cases the reactor was found to be operating well outside the regime where external mass transfer limitations apply. Presumably the observed decline in methane conversion rate with increasing contact time results from operating the reactor in an integral mode where the variation in W/F results in different average reactant and product concentrations and hence different reaction rates. The possibility of rate suppression by one or more of the products reducing catalyst activity must also be considered.

3.2 Methane conversion and product selectivity

Methane conversion (percentage of input methane converted to products), oxygen consumption (percentage of input O_2 consumed) and product selectivity (amount of input methane converted to a specific product as a percentage of total methane converted) for feed gases containing 1.1 and 9.4% O_2 are illustrated in Fig. 2 as a function of W/F. At the lower O_2 concentration (Fig. 2a), total O_2 consumption was achieved at the longest contact time when CH_4 conversion reached 3%. Selectivity to hydrocarbons was very high at 94% for W/F = 0.3, of which 91% corresponded to C_2 hydrocarbons and 3% C_3 hydrocarbons, principally propane. At total O_2 consumption, hydrocarbon selectivity was still high at 93% with C_3 's increasing to 5% and consisting principally of propylene. Increasing contact time resulted in an increasing conversion to ethylene with a corresponding decrease in ethane. Carbon dioxide was the dominant carbon oxide product.

With 9.4% O_2 in the feed gas (Fig. 2b) the selectivity to hydrocarbons showed a strong dependence on contact time, declining from 85% at W/F = 0.3 to 76% at 1.5. C_3 hydrocarbons, mainly propylene, reached 6% at the longer reaction times. The loss in hydrocarbon selectivity appears to be due to an increasing contribution from secondary reactions in the presence of a higher O_2 concentration and is reflected in increasing selectivity to carbon oxides. This is accompanied by an increased production of ethylene and decline in ethane.

Minor yields of other hydrocarbons were observed, including butenes, butadiene and, at higher temperatures, benzene, toluene and acetylene. These products all demonstrate an increasing contribution from secondary gas phase reactions as operating conditions became more severe. Hydrogen was also observed in the product stream in amounts equivalent to about 15% of the hydrogen liberated by the methane conversion and also depended upon reaction severity. Hydrogen could arise by pyrolysis of ethane to ethylene or possibly by decomposition of reaction intermediates such as formaldehyde.

The dependence of CH_4 conversion, O_2 consumption and product selectivity on O_2 concentration in the feed gas is summarised in Fig. 3 for a fixed W/F value of 1.5. Hydrocarbon selectivity declined linearly with increasing O_2 concentration in the feed gas (CH_4 constant at 90%) accompanied by increasing formation of carbon oxides. Ethane selectivity declined rapidly with increasing O_2 concentration whereas ethylene increased and eventually reached a plateau of 42%. In other experiments where total O_2 consumption was achieved, ethylene selectivity reached a maximum and then declined with increasing contact time suggesting that secondary, undesired production of carbon oxides adversely affected ethylene production. O_2 consumption showed a small decrease with increasing O_2 content whereas CH_4 conversion increased markedly, reaching 11% with 9.4% O_2 in the feed gas.

3.3 Reaction sequence

Ito et al. (5,6) proposed that the initial step in the catalytic conversion was the formation of a methyl radical by hydrogen abstraction from a methane molecule at a

thermally generated $[\text{Li}^+\text{O}^-]$ site. Recombination of two methyl radicals either on the surface or in the gas phase produced ethane. Ethylene was thought to arise from partial oxidation or pyrolysis reactions of ethane. Carbon oxides arose from either oxidation of methyl radicals or further oxidation of C_2 products.

In an attempt to clarify the reaction sequence, experiments were conducted at short pseudo-contact times using a small catalyst bed (<0.5 g) in order to examine the product distribution at low extents of reaction. Figure 4 shows the dependence on temperature of CH_4 conversion, O_2 consumption and product selectivity at a fixed W/F of 0.05 using a 50% CH_4 /5% O_2 /45% He feed gas mixture. Clearly at temperatures below about 700°C CH_4 conversion and O_2 consumption were low, C_2 hydrocarbon selectivity was also low and carbon oxides were the major products below about 650°C. Increasing the temperature resulted in increasing C_2 selectivity, which reached a broad maximum of 75% between 750 and 800°C. Below 650°C ethane was the only hydrocarbon species, with selectivity to ethylene increasing at higher temperatures. These data suggest that, at least in the early stages of the reaction, ethane and carbon oxides are formed by parallel rather than sequential reactions. The reactions involved must have different activation energies, resulting in a changing product distribution with increasing temperature.

Further evidence in favour of this reaction sequence is depicted in Figure 5. These data were derived at short residence times (W/F = 0.01-0.1) with a feed gas consisting of 95% CH_4 /5% O_2 . Product selectivities are shown as a function of methane conversion, and the diagram includes a curve representing O_2 consumption. At the higher conversions C_2 selectivity started to decline and carbon oxides to increase owing to secondary oxidation as the oxygen consumption approached 100%. However, extrapolation of the selectivities back to zero conversion provides evidence of the primary reaction products without contribution from secondary processes. In this example and in all other experiments only ethane and carbon oxides formed intercepts. Ethylene and C_3 hydrocarbon selectivities extrapolate to zero at zero CH_4 conversion indicating that these products arise from secondary reactions of ethane. The increase in carbon oxides at higher conversion must be associated with further oxidation of product hydrocarbons.

The simultaneous formation of ethane and carbon oxides again suggests that in the early stages of the reaction these products arise from parallel rather than sequential reactions. There is thus no direct route to ethylene. These so-called 'primary selectivities' at zero conversion are considered to be an intrinsic property of the catalyst and as such provide a useful means of comparing the performance of different catalysts.

CONCLUSIONS

Product selectivity from the catalytic partial oxidation of methane over a Li/MgO catalyst is very dependent on contact time, O_2 concentration and temperature. Very high selectivities to hydrocarbons ($>90\%$) can be achieved provided high $\text{CH}_4:\text{O}_2$ ratios ($>50:1$) are used. The reaction sequence involves the initial formation of ethane and carbon oxides via parallel reactions. There is no direct route to ethylene, which arises from secondary reactions of ethane.

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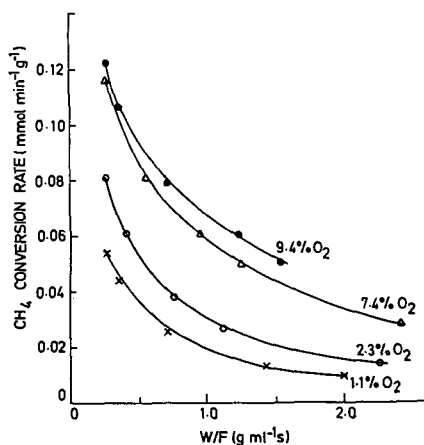


Figure 1. Influence of pseudo-contact time and oxygen level in feed gas on methane conversion rate at 770°C (feed gas 90% CH₄)

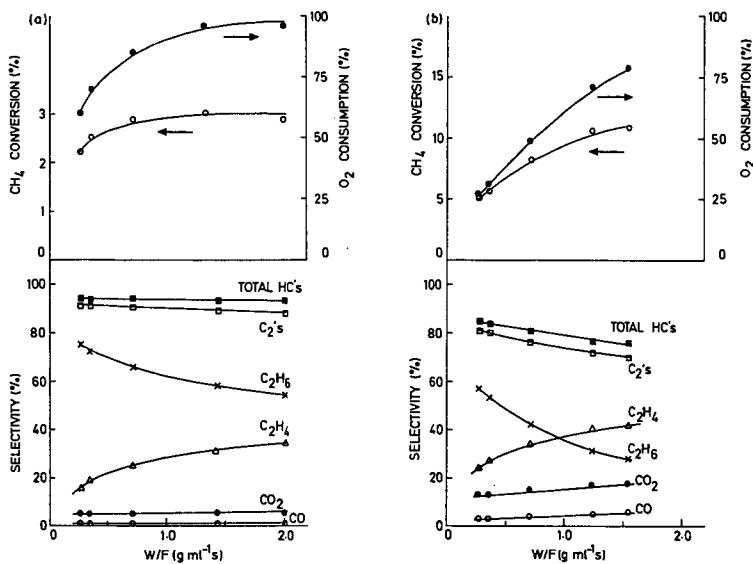


Figure 2. Influence of pseudo-contact time on methane conversion, oxygen consumption and product selectivities at 770°C. (a) Feed gas 1.1% O₂, 90% CH₄. (b) Feed gas 9.4% O₂, 90% CH₄

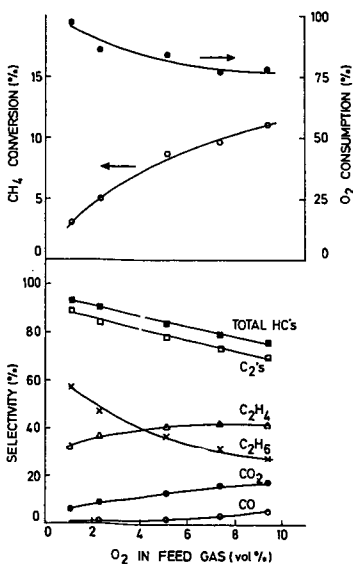


Figure 3. Influence of oxygen level in feed gas on methane conversion, oxygen consumption and product selectivities at 770°C (W/F = 1.5 g ml⁻¹s)

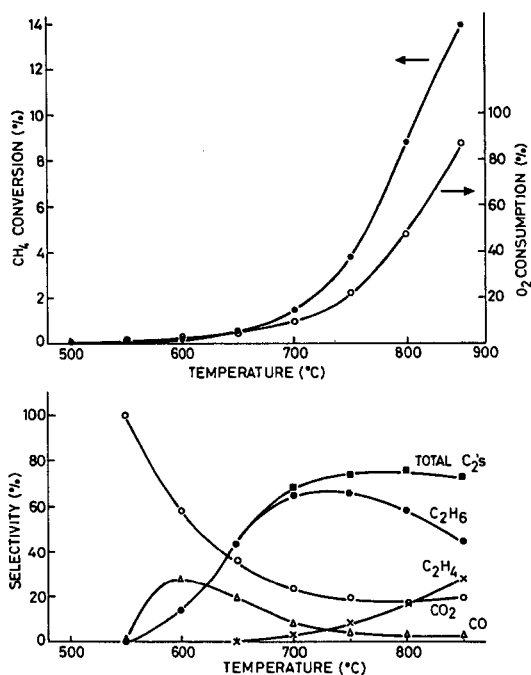


Figure 4. Effect of temperature on methane conversion, oxygen consumption and product selectivity (feed gas 50% CH₄, 5% O₂)

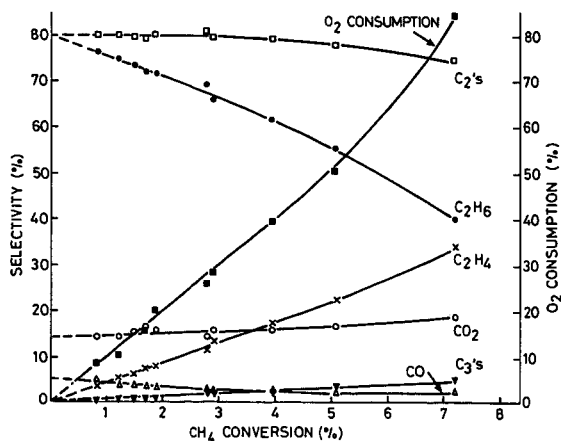


Figure 5. Variation of product selectivity and oxygen consumption with methane conversion at 750°C (feed gas 95% CH₄, 5% O₂)